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Brightness Reversion of Mechanical Pulps
Part XIII: Photoinduced Degradation of Lignin on Cellulose Matrix

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BRIGHTNESS REVERSION OF MECHANICAL PULPS PART XIII: PHOTOINDUCED DEGRADATION OF LIGNIN ON CELLULOSE MATRIX

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ABSTRACT

An acidic dioxane extraction procedure was employed to isolate lignin from softwood bleached chemithermomechanical pulp (BCTMP). The isolated lignin was characterized spectroscopically and applied on cellulose testsheets. The treated cellulose testsheets were shown to exhibit photoyellowing properties comparable to BCTMP. The photolyzed lignin was re-isolated and characterized by using spectroscopic techniques. The UV-VIS and FT-IR studies implied the elimination of guaiacyl structure of lignin and the formation of the carboxyl and/or unconjugated carbonyl groups during the photoyellowing process. The steady-state emission intensity of the excited states of guaiacyl structures decreases with increasing photolysis time, suggesting the formation of quinones during photolysis. NMR analysis of the photolyzed lignin indicated that the formyl, methoxy, and uncondensed phenolics decrease in concentration as the irradiation proceeds. In contrast, condensed lignin and carboxylic acids increase as photolysis time is increased. These results are explained within the mechanism of lignin photodegradation.

INTRODUCTION

High-yield mechanical pulping is an attractive technology for addressing

many of the challenges of modern papermaking operations. The production of high-yield pulps provides a valuable furnish with little environmental impact, improved wood utilization practice, and simplified manufacturing techniques. Unfortunately, the well-known photoyellowing properties of mechanical pulp have hindered additional usage of this valuable furnish.[1]

The photoyellowing of mechanical pulp is generally attributed to the lignin component of the fiber. Although the exact mechanism of photoyellowing is not fully understood, substantial advancements have been made in this field of wood chemistry over the last two decades.[1-3] It is generally believed that several subunits of lignin, including stilbenes, conjugated phenolics, coniferyl aldehyde, α-carbonyl-β-O-aryl structures, and catechols, can absorb near ultraviolet light (λ: 300-400 nm) eventually resulting in the photoformation of chromophores in the visible spectrum.[2] *Para-* and *ortho*-quinones have been detected in irradiated pulp and are believed to contribute to the discoloration of mechanical pulp along with other color bodies. Inasmuch as these photoproducts are formed in small amounts and are difficult to isolate from irradiated mechanical pulp, a variety of model systems have been employed to study the photodegradation of lignin. This report examines the photodegradation properties of lignin extracted from BCTMP pulp and photolyzed with near-UV light.

EXPERIMENTAL

Materials

All reagents and solvents were commercially purchased and used as received. A commercial softwood BCTMP, impregnated and bleached with hydrogen peroxide, was employed for all studies in this report. Whatman # 3

filter paper was used as cellulose testsheets. All water used in this report was initially deionized and then subsequently purified through a Ultrapure Water System.

Instrumentation

All NMR spectra were recorded on a 400 MHz Bruker DMX spectrometer at 25°C. A Perkin-Elmer 320 UV-VIS spectrophotometer was used to measure the absorption spectra. FT-IR spectroscopy was carried out with a Nicolet 550 spectrometer at room temperature. The emission spectra were performed with a Perkin-Elmer LS-5B luminescent spectrometer (λ_{ex}= 280 nm). The photoageing experiments were performed with a Rayonet Photochemical Reactor (RPR-100) with sixteen black lamps (λ_{max}: 350 nm). A fan located at the bottom of the photochemical reactor was employed to maintain a photolysis temperature of <30°C. A Technidyne Brightimeter Micro S-5 was used to measure the TAPPI brightness of each testsheet according to TAPPI procedure T452 om-92.[5]

Procedures

Isolation of lignin from BCTMP.[6] Before isolation of the lignin, the softwood BCTMP was Soxhlet extracted with acetone for 24 h. The dry pulp (150 g) was then refluxed in a 0.01 N HCl dioxane-water (3 L, 8.5:1.5) solution under argon for 1 h. The pulp was filtered and washed with fresh dioxane (200 mL × 3). The combined aliquots were neutralized with powder $NaHCO_3$, filtered, and concentrated under reduced pressure at ~ 45°C. The concentrated solution was added to 700 mL of a 0.006 N aqueous HCl and the precipitated lignin was twice

washed with acidified water (pH 2-3) and then freeze-dried. The lyophilized lignin was subsequently dried under high vacuum (~ 0.006 Torr) at 50°C for at least 24 h. The yield of lignin was calculated to be 0.7% based on the mass of pulp initially used (% lignin yield = mass of lignin isolated/mass of lignin in pulp).

Filter papers treated with lignin. Cellulose testsheets (~ 150 g/m^2) were sprayed with a 9:1 dioxane-water solution (5 mL) containing BCTMP lignin (0.0870 g). The treated handsheets were dried overnight in the absence of light prior to irradiation.

UV photolysis of the treated filter papers. Four lignin-impregnated cellulose testsheets were attached to a merry-go-round and photolyzed in a Rayonet RPR-100 photochemical reactor at ~30°C. Each side of the paper was photolyzed for half the photolysis period. At selected time periods, the irradiated testsheets were removed from the reactor and equilibrated to a constant temperature of 22°C (± 2.0°) and a relative humidity of 50% (± 2.0%) for 4 h prior to measuring TAPPI brightness values.[5]

Extraction of the photolyzed lignin. The photolyzed filter papers were extracted with 9:1 dioxane-water mixture (100 mL × 3). The combined extracts were filtered and concentrated under reduced pressure at 45°C. The photolyzed lignin was freeze-dried and then further dried with a high vacuum pump at 50°C for 24 h. This procedure typically yielded 83-99% lignin recovery (see Table 1).

Quantitative ^1H NMR spectroscopy. Functional group analysis of the residual lignin samples was accomplished, in general, following Lundquist's procedure of analyzing lignin (0.0150 g) in dry DMSO-d_6 (0.50 mL).[7] As a slight

modification to this literature procedure, we employed sodium-3-trimethylsilyl propionate-2,2,3,3-d_4 (0.0480 g) as an internal standard to quantify functional groups.[8]

TABLE 1: Recovery of Lignin from Cellulose Testsheets.

Period Irradiation, min	Mass Recovery,[a] %
0.0	99
1.0	99
2.0	97
4.0	93
8.0	91
30.0	88
60.0	83

[a] calculated by determining initial mass of lignin applied onto testsheet and mass of lignin recovered after *p*-dioxane extraction.

FT-IR spectroscopy. Lignin samples (0.1 mg) were mixed with KBr powder (0.20 g) and immediately analyzed. Typical spectral data were accomplished with 128 scans/sample at room temperature. Background spectra were collected with a pure KBr pellet.

UV-VIS spectroscopy. Lignin samples (0.18 mg) were dissolved in 9:1 dioxane-water mixture (100 mL) and the spectra (λ: 200-800 nm) were recorded immediately thereafter at room temperature; absorption at 280 nm was also measured.

Emission spectroscopy. The lignin solutions that were used in UV-VIS absorption spectrum measurements were subsequently used to determined the emission spectrum by steady-state excitation at 280 nm.

RESULTS AND DISCUSSION

The fundamental photoyellowing chemistry of mechanical pulp has been frequently studied with lignin model compounds.[1,9] These investigations have established many of the fundamental reactions believed to be involved in the photoyellowing process. To further broaden our knowledge of the mechanisms of brightness reversion, several researchers have begun to examine the photochemistry of isolated lignin. The most common source of lignin studied to date is milled wood lignin (MWL). Destiné *et al.*[10] demonstrated that the photodegradation of MWL is influenced by the presence of oxygen; whereas Agrolpoulos[11] noted that changes in functional groups of milled wood lignin were dependent upon the period of irradiation.

Isolation of lignin from BCTMP. Gellerstedt *et al.*[12] employed a mildly acidic aqueous dioxane solution (pH 4) to relinquish the end-groups of mechanical pulp lignin and examined their photochemistry. To facilitate the release of additional lignin, we examined the use of a more acidic aqueous dioxane solution (pH 2) to extract additional lignin from BCTMP.

The extraction of lignin from a softwood BCTMP was accomplished using a modification of the acidic dioxane extraction procedure that has been commonly employed to recover lignin from kraft pulps. One of our primary considerations for the lignin isolation procedure was to extract lignin from BCTMP without significantly introducing new chromophores in the visible range. A series of

preliminary studies indicated that these concerns were best addressed refluxing BCTMP pulp in a 0.01 N HCl 9:1 dioxane-water solution for 1 h under an argon atmosphere.

Photoreversion properties of isolated lignin. To determine if the lignin isolated from the BCTMP fibers exhibited brightness reversion properties, the extracted lignin was redissolved in an aqueous dioxane solution and applied onto cellulose testsheets. Initially, we examined several levels of applications of lignin (0.5–5% by weight) onto cellulose testsheets. The treated testsheets were irradiated with a 300–400 nm light source and TAPPI brightness measurements were periodically taken. The photoreversion properties of these testsheets are summarized in Figure 1, and these data demonstrate that the lignin impregnated cellulose testsheets exhibit brightness reversion properties. These results also suggested that the photoreversion properties of these testsheets approach an asymptotic reversion limit near 5% lignin applied onto a cellulose testsheet.

The photoreversion properties of the 3% lignin-cellulose testsheets were then evaluated against BCTMP and acid hydrolyzed BCTMP testsheets. In addition, the extracted lignin (3% by weight) was applied to testsheets prepared from the acidolysis treatment of BCTMP pulp. Figure 2 summarizes the changes in TAPPI brightness as these testsheets were irradiated with a 300–400 nm light source for varying time periods. All the testsheets exhibited comparable brightness reversion properties consisting of a very fast reversion phase (*ca.* first 15 min of irradiation) and a subsequent slower phase.

Characterization of post-photolyzed lignin. To study the photo-degradation of BCTMP lignin, the irradiated testsheets were extracted with *p*-dioxane. Table 1 summarizes the mass recovery of lignin after irradiation. In general, the mass recovery of lignin was above 90% but did decrease as the

photolysis time was increased, suggesting the photoproducts of lignin might be chemically and/or physically incorporated into the cellulose matrix.

^{1}H NMR analysis. NMR analysis of lignin is a facile means of analyzing many of the structural components of lignin. Lundquist[7] has shown that underivatized lignin can be quantitatively analyzed by ^{1}H NMR for a variety of functional groups. The ^{1}H NMR of the extracted lignin from BCTMP is shown below in Figure 3. This spectrum has structural features that are similar to one isolated from softwood pulp reported by Lundquist[13] and Akerback *et al.*[14]

Employing this procedure for the lignins recovered in Table 1, the content of methoxy, aromatic, condensed and non-condensed phenolic, formyl, and acidic groups could be readily determined. The results of these analyses are summarized in Figures 4 to 6.

Figure 4A shows that a component of the uncondensed phenolic units in lignin are rapidly consumed in the early stages of the photolysis experiment. Interestingly, the loss of uncondensed phenolics is accompanied by an increase in the overall amounts of condensed phenolics (see Figure 4B). It is well known that unstable phenolic radicals can easily undergo dimerization[15] and a comparable mechanism is most likely contributing to the formation of condensed phenolics observed in Figure 4B. The loss of aromatic protons (see Fig. 5A) as the lignin samples are irradiated is also consistent with a condensation mechanism, although other mechanism(s) could also contribute to this phenomenon. The loss of methoxy groups (see Fig. 5B) during photolysis has been previously noted by Leary[16] when mechanical pulp was irradiated; our results are consistent with these results.

Accompanying the photoinitiated loss of phenolic groups is an increase in the acid content of the photolyzed lignin, as shown in Figure 6. The increase in acidic groups (see Fig. 6A) during photolysis is supportive of the overall oxidative

mechanisms that have been suggested during the photoyellowing of mechanical pulp. The loss of formyl groups (see Fig. 6B) during photolysis can be attributed, at least in part, to simple oxidation of the corresponding acid.

FT-IR spectroscopy. FT-IR analysis of the isolated lignin samples provided an alternative means of characterizing the changes in lignin during photolysis. As shown in Figure 7, several FT-IR signals of lignin are modified during irradiation.

The signal at 1726 cm^{-1} is very prominent in the irradiated lignin; whereas in the IR spectra of non-photolyzed lignin, this signal is substantially diminished. This IR band has been assigned to carbonyl group of carboxyl and unconjugated carbonyl groups (conjugated carbonyl absorbs at 1715-1680 cm^{-1}).[17-18] Agarwal *et al.*[19] had notably similar trends when using FT-IR to characterize photoyellowed TMPs. Our results suggest that the isolated lignin from softwood BCTMP must undergo a rather rapid oxidation process, in the early phase of brightness reversion.

As reported by Schultz,[18] quantitative analysis of IR spectra can be determined upon the signal at 1600 cm^{-1}. This signal, due to an aromatic C-H stretch, provides a facile means of correlating signals measuring relative signal intensities. The ratio of absorbencies from 1726 cm^{-1} to 1600 cm^{-1} for the untreated and photolyzed lignins are summarized in Figure 8. Unfortunately, these results can be viewed as only semiquantitative since the NMR analysis suggests that a portion of aromatic C-H groups in lignin are decreasing upon photolysis.

Nonetheless, the FT-IR analyses are consistent with the NMR results, suggesting that acid groups increase with increasing irradiation time. Both spectroscopic techniques suggest that there is a fast and slow phases to the photooxidation of lignin.

UV-VIS spectroscopy. Absorption spectra of lignin were measured in a 9:1 dioxane-water mixture as a function of photolysis time. A new band with maximum at 280 nm, a shoulder at 240 nm, and a sharp peak at 220 nm were observed as the period of irradiation was extended. These absorption bands are in good agreement with studies reported by Lin *et al.*[20] for softwood MWL lignin. The change in the 280 nm absorption band during UV irradiation is given in Table 2. This band (280 nm) decreases as the photolysis time is increased. There is no shift in absorption maximum, suggesting no contribution from the photoproducts. The decrease in absorbance at 280 nm may be consistent with the brightness loss, *i.e.* the formation of chromophores. It is believed[21-22] that the maximum at 280 nm is attributed to the absorption of phenylpropane (or guaiacyl structure), a basic structural unit of lignin. The elimination of the phenylpropane structure upon the photolysis is consistent with the formation of acid and/or the loss of aromatic protons observed with NMR in this study.

TABLE 2: Absorbance at 280 nm and Relative Fluorescent Emission Intensity at 360 nm of the Extracted Lignin as a Function of Photolysis Time.

Time, min	Abs.	Relative Em. Intensity
0.0	0.328	1.0
1.0	0.258	0.86
2.0	0.242	0.82
4.0	0.221	0.89
8.0	0.232	0.80
30.0	0.192	0.57
60.0	0.204	0.58

Emission spectroscopy. The solutions used in UV-VIS absorption measurement were also employed in the measurement of emission spectra. The results are given in Table 2. The emission intensity at maximum of 360 nm decreases as the photolysis time is increased. It is noted that the absorbance at 280 nm decreases as photolysis time is increased (see Table 2). If we assume that the decrease in absorbance at 280 nm is due to the degradation of lignin and no contribution is due to the absorption from photoproducts, the conclusion can be made that the decrease in emission intensity is mainly due to the decrease in absorbance. This is because the less photons absorbed by lignin, *i.e.*, lesser number of excited molecules, the less photons will emit. Since the photoproducts, such as quinone structures, have no emission at 280 nm excitation,[23] the decrease in the emission intensity may suggest that the formation of the quinones increases with increasing irradiation time.

CONCLUSIONS

Lignin isolated from softwood BCTMP under mild acid hydrolysis conditions (pH 2) exhibits brightness reversion properties. As a result, the isolated lignin can be used as a model in the study of brightness reversion of mechanical pulp. The photoproducts of lignin might chemically and/or physically incorporate into the cellulose fiber during photoyellowing. The increase in condensed lignin and carboxylic acids during photolysis is attributed to the photooxidation of lignin, which is consistent with the decrease in the formyl, methoxy, and uncondensed phenolics in lignin. The changes in functional groups during UV irradiation may play an important role in understanding the mechanism of brightness reversion of mechanical pulps.

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FIGURE CAPTIONS

FIGURE 1. TAPPI Brightness of the testsheets treated with several levels of applications of lignin (0.5–5% by weight) as a function of photolysis time.

FIGURE 2. TAPPI Brightness as a function of photolysis time for testsheets prepared from: (●) BCTMP; (○) refluxing BCTMP in an aqueous dioxane solution (pH 2.0) for 60 min under argon; (▼) cellulose and testsheet treated with 3% lignin; (▽) refluxing BCTMP in an aqueous dioxane solution (pH 2.0) for 60 min under argon and testsheet treated with 3% lignin.

FIGURE 3. NMR spectrum of the isolated BCTMP lignin (15 mg) without irradiation in dry DMSO-d_6 (0.50 mL).

FIGURE 4. Number of mole of proton for condensed and uncondensed phenolic units in lignin as a function of photolysis time.

FIGURE 5. Number of mole of proton for methoxy and aromatic units in lignin as a function of photolysis time.

FIGURE 6. Number of mole of proton for formyl and acidic units in lignin as a function of photolysis time.

FIGURE 7. FT-IR spectra of unphotolyzed and photolyzed lignin.

FIGURE 8. FT-IR relative intensity (1726/1600 cm^{-1}) as a function of photolysis time.

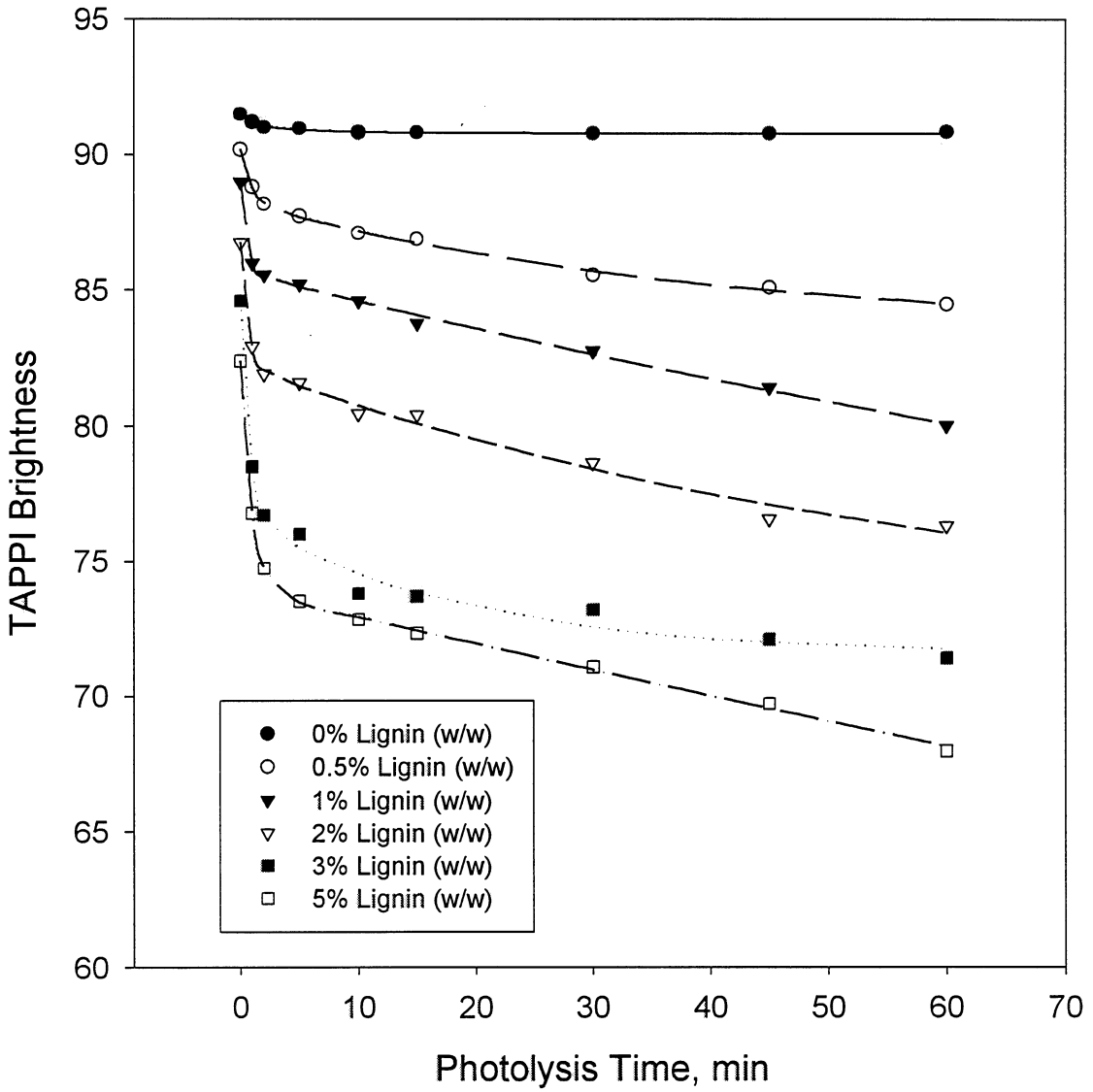

95
90
85
80
75
70
65
60
TAPPI Brightness
0
10
20
30
40
50
60
70
Photolysis Time, min
0% Lignin (w/w)
0.5% Lignin (w/w)
1% Lignin (w/w)
2% Lignin (w/w)
3% Lignin (w/w)
5% Lignin (w/w)

Figure 1

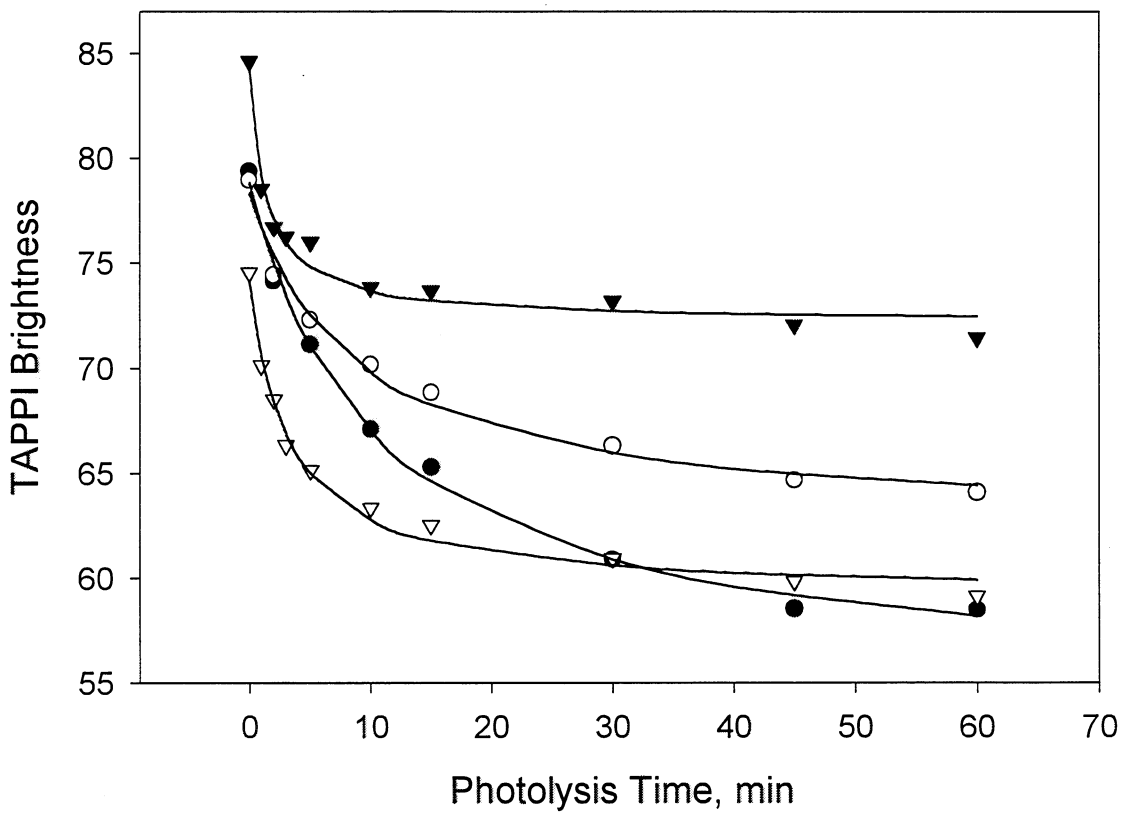

TAPPI Brightness
85
80
75
70
65
60
55
0
10
20
30
40
50
60
70
Photolysis Time, min

Figure 2

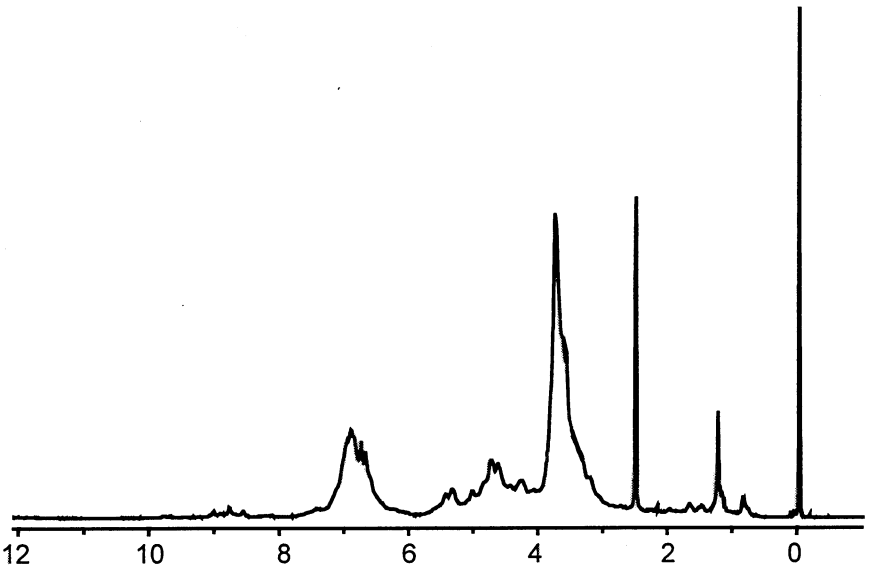
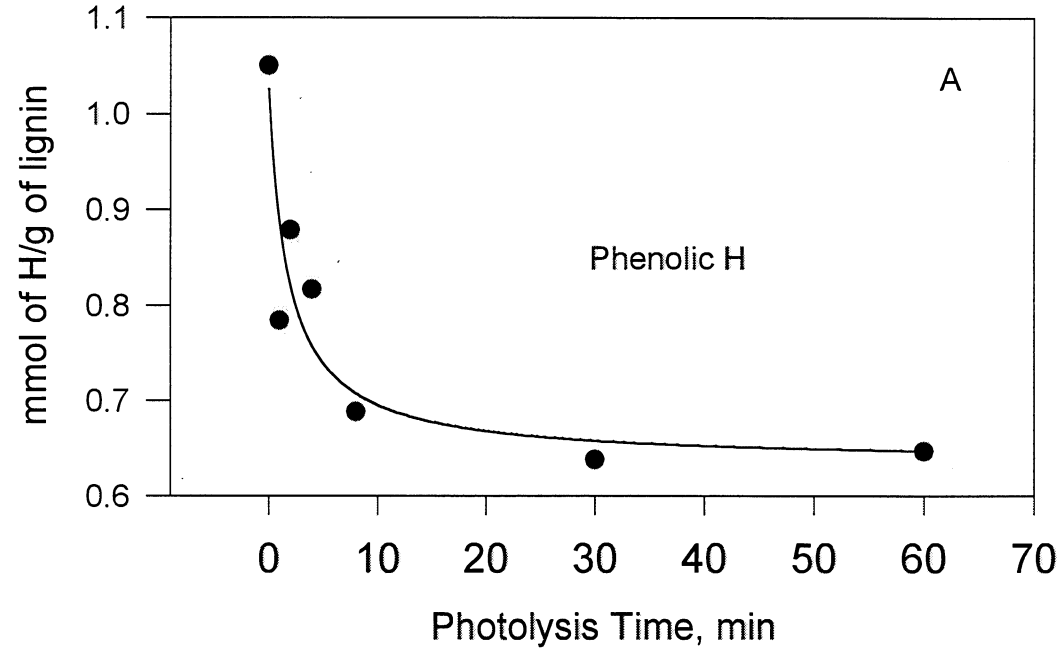


Figure 3


1.1
1.0
0.9
0.8
0.7
0.6
mmol of H/g of lignin
A
Phenolic H
0
10
20
30
40
50
60
70
Photolysis Time, min

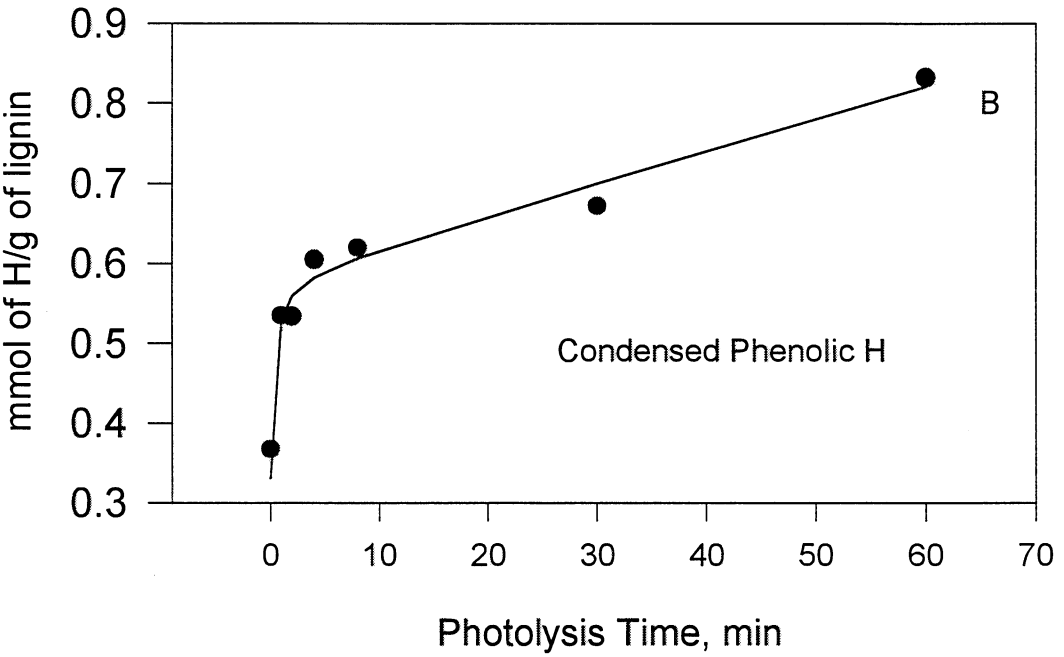
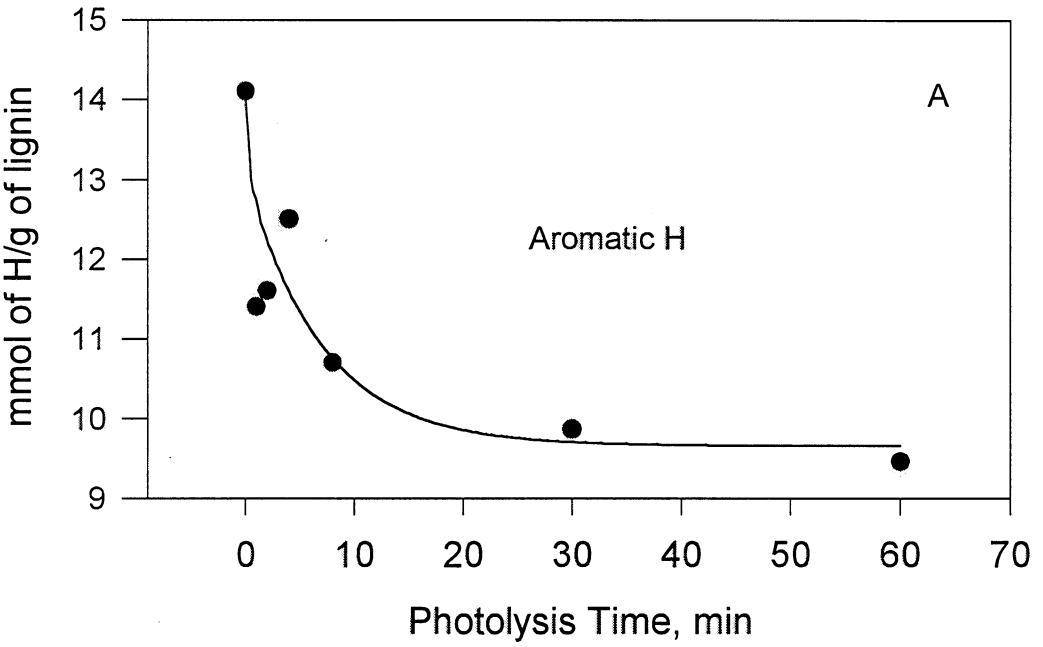

0.9
0.8
0.7
0.6
0.5
0.4
0.3
mmol of H/g of lignin
B
Condensed Phenolic H
0
10
20
30
40
50
60
70
Photolysis Time, min

Figure 4


15
14
13
12
11
10
9
mmol of H/g of lignin
A
Aromatic H
0
10
20
30
40
50
60
70
Photolysis Time, min

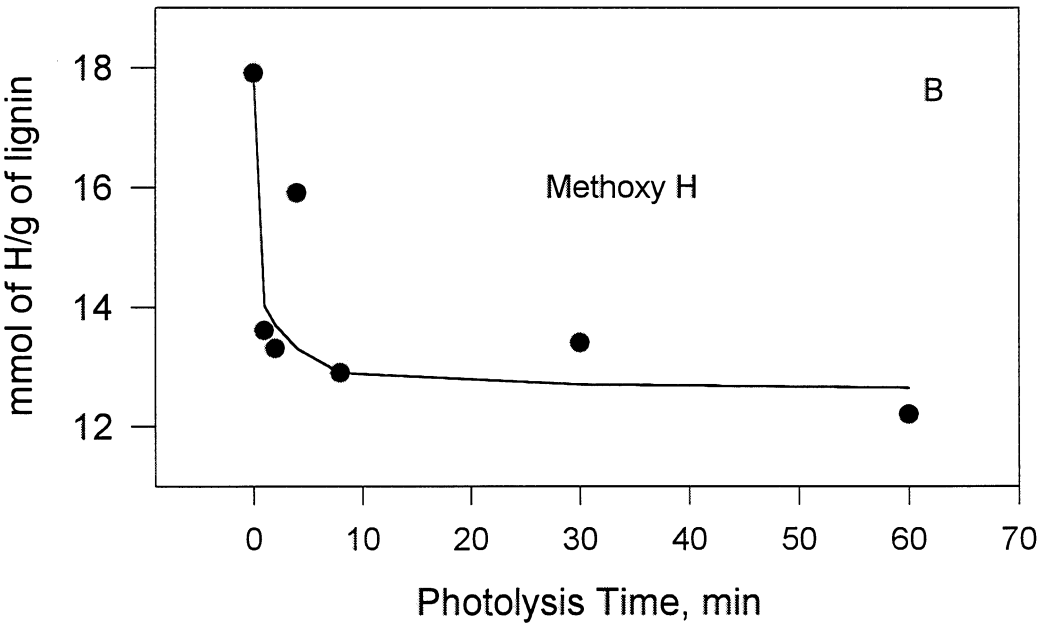
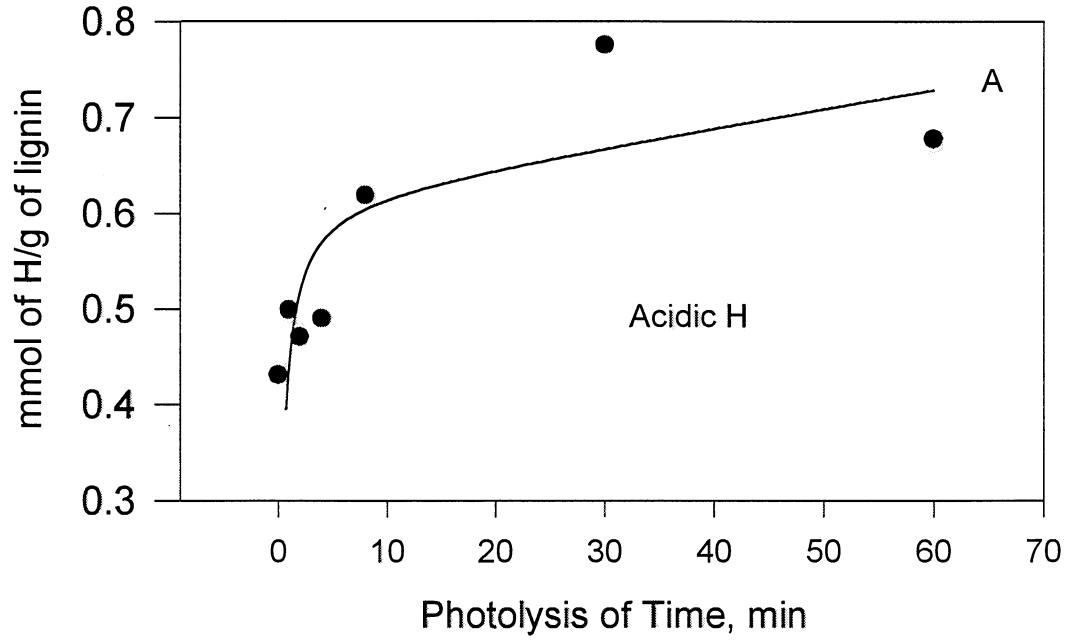

18
16
14
12
mmol of H/g of lignin
B
Methoxy H
0
10
20
30
40
50
60
70
Photolysis Time, min

Figure 5


0.8
0.7
0.6
0.5
0.4
0.3
mmol of H/g of lignin
A
Acidic H
0
10
20
30
40
50
60
70
Photolysis of Time, min

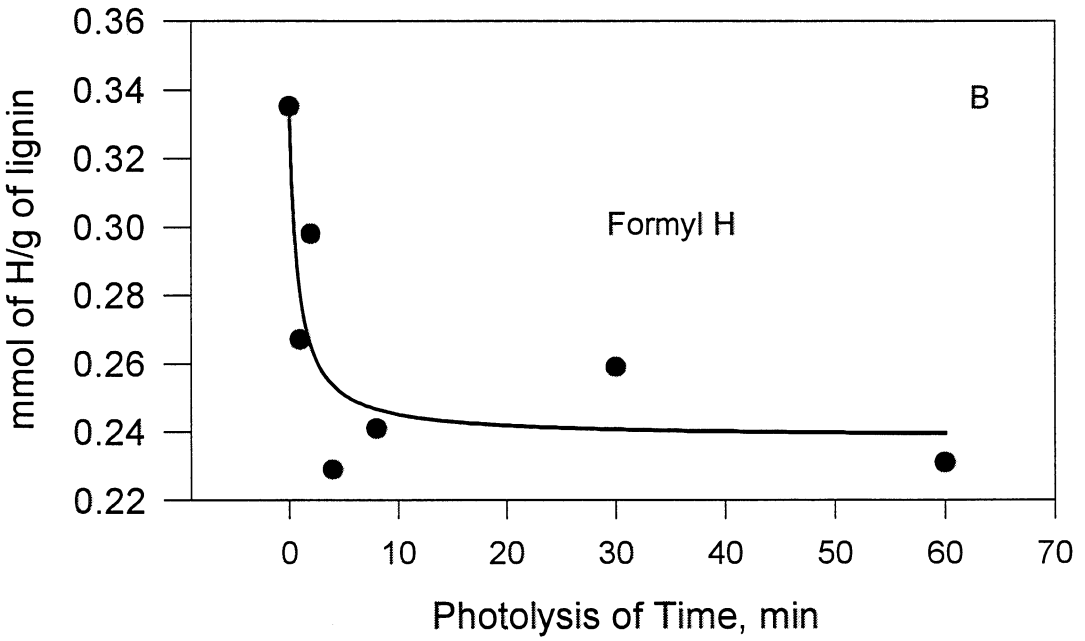

0.36
0.34
0.32
0.30
0.28
0.26
0.24
0.22
mmol of H/g of lignin
B
Formyl H
0
10
20
30
40
50
60
70
Photolysis of Time, min

Figure 6

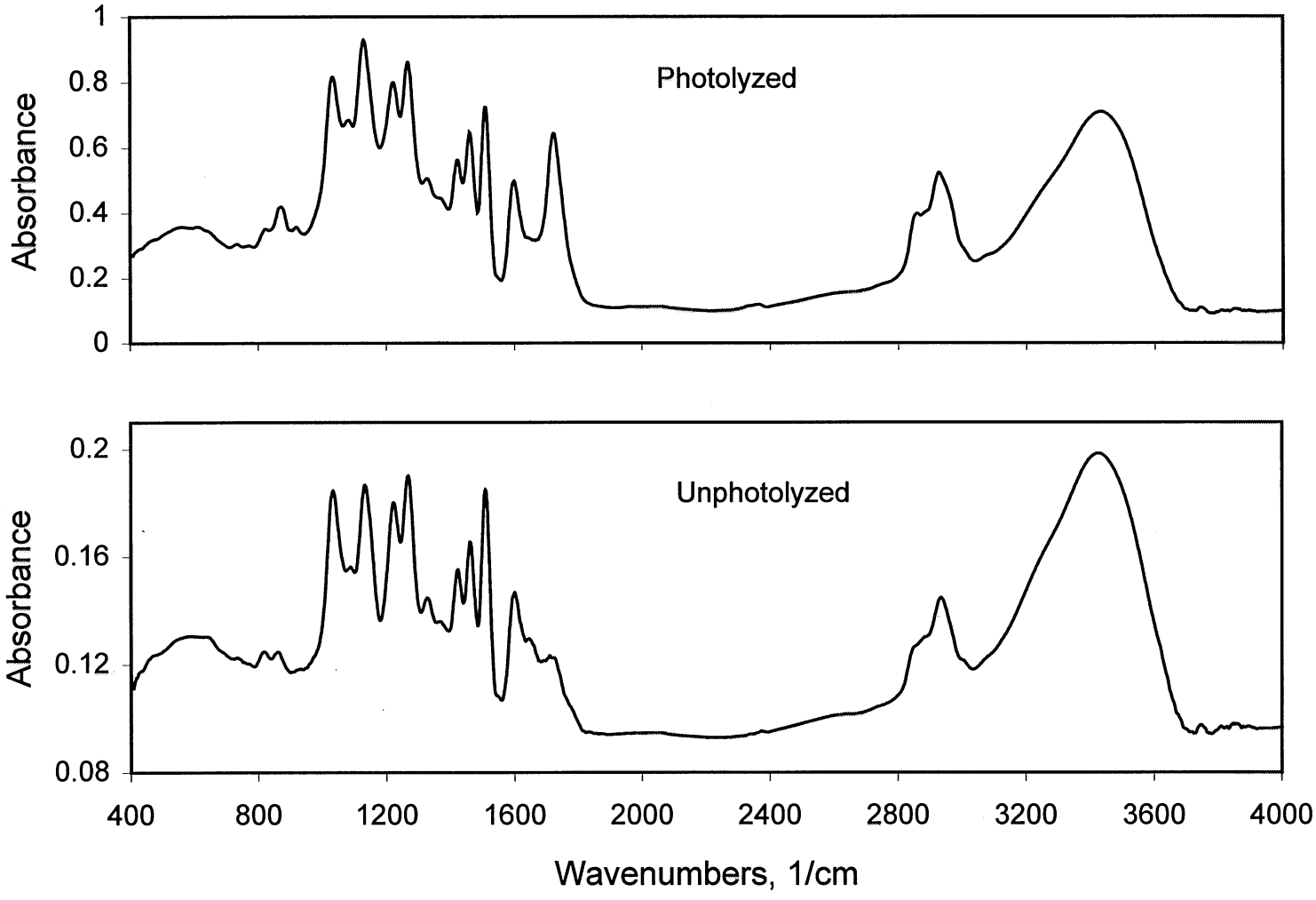

Photolyzed
Absorbance
1
0.8
0.6
0.4
0.2
0
Unphotolyzed
Absorbance
0.2
0.16
0.12
0.08
400
800
1200
1600
2000
2400
2800
3200
3600
4000
Wavenumbers, 1/cm

Figure 7

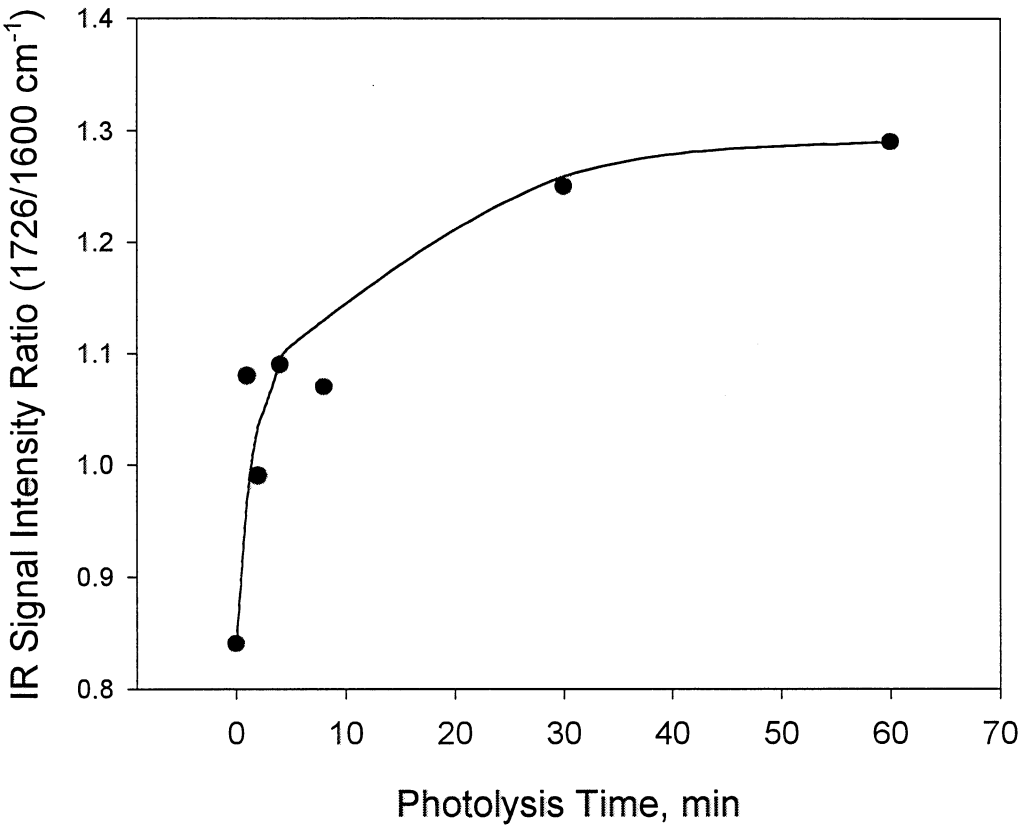

IR Signal Intensity Ratio (1726/1600 cm-1)
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0
10
20
30
40
50
60
70
Photolysis Time, min

Figure 8